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(41) A reexamination of the IR spectra of Me_2Se,[38] Me_2SeCl_2 (benzene solution),[29,39] and Me_2SeBr_2 (benzene solution)[39] suggests that the previous assignments[20] for ν_{sym} (280 (s) cm^{-1}) and ν_{asym} (244 (vs) cm^{-1}) for Cl–Se–Cl modes in Me_2SeCl_2 should be reversed. It is now proposed that the coincidence of the C–Se–C deformation, which occurs in Me_2Se[38] at 233 cm^{-1} (Raman) and at 238 cm^{-1} (m, sh) (IR) in Me_2SeBr_2,[39] with the Cl–Se–Cl mode at 244 cm^{-1} leads to an enhanced intensity for this lower frequency absorption. This resulted in an incorrect assignment to ν_{asym}(ClSeCl); it is now assigned to ν_{sym}(ClSeCl) + ν_{def}(CSeC). The absorption at 280 cm^{-1} is assigned to ν_{asym}(ClSeCl). In the solid state Me_2SeCl_2 exhibits a very broad and structureless absorption envelope in the Se–Cl region. We also note that in contrast to the Raman spectrum of the solid[38] the far-IR spectrum of Me_2TeCl_2 in benzene solution is interpretable in a standard fashion, i.e., $\nu_{asym}(ClTeCl) > \nu_{sym}(ClTeCl)$. Absorptions ($cm^{-1}$) and assignments: 265 (vs) (ν_{asym}(ClTeCl)), 223 (s) (ν_{sym}(ClTeCl)), 188 (w) (ν_{def}(CTeC)), 124 (ms) (ν_{def}(ClTeCl)); other absorptions are at 87 (wm) and 55 (w, br). Finally, we add that the IR spectrum of Me_2TeBr_2 in benzene confirms previous assignments:[38] 190 (s) (ν_{asym}(BrTeBr)), 166 (w, sh) cm^{-1} (ν_{sym}(BrTeBr)).

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Chirality of Oxidized and Reduced Octadecamolybdodiphosphate Anions. Observation of a Pfeiffer Effect

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Recently determined structures of $P_2Mo_{18}O_{62}^{6-}$ and α-$P_2W_{18}O_{62}^{6-}$ show that the molybdate has only D_3 symmetry and is therefore chiral. The infrared spectra of both complexes in the solid state and in acetonitrile solution are reported and they confirm that the chirality of the molybdate is not caused by crystal packing forces. Solutions of the tetrabutylammonium salt of the heteropolymolybdate in acetonitrile in the presence of *l*-brucine sulfate show a significant positive Cotton effect centered at 350 nm ($[M]_{380} = +1.4 \times 10^3$ deg dm^{-1} M^{-1}). This behavior is attributed to a Pfeiffer effect since analogous measurements with the nonchiral polyanions α- and β-$P_2W_{18}O_{62}^{6-}$, α-$SiMo_{12}O_{40}^{4-}$, and $Mo_6O_{19}^{2-}$ show only minor amounts of induced optical activity. The heteropoly blue $H_2P_2Mo^{V}{}_2Mo_{16}O_{62}^{6-}$ also exhibits a Pfeiffer effect but of diminished magnitude and no optical activity is associated with the intervalence charge-transfer transitions. An explanation of this behavior and of the apparent nonexistence of odd reduction states of $P_2Mo_{18}O_{62}^{6-}$ is presented.

We recently pointed out[1] that, according to the results of careful x-ray structural analyses,[2,3] the heteropolyanion $P_2Mo_{18}O_{62}^{6-}$ ("P_2Mo_{18}") is chiral in a particularly subtle fashion. Although the structure of P_2Mo_{18} is conventionally represented as an assemblage of edge- and corner-sharing MoO_6 octahedra and PO_4 tetrahedra, with an apparent overall point symmetry D_{3h} (see Figure 1a), displacements of molybdenum atoms within their respective MoO_6 octahedra lower the total symmetry to D_3. The displacements, illustrated in Figure 1b, give rise to loops of Mo–O–Mo bonds that are alternately "short" (~1.80 Å) and "long" (~2.05 Å). The chirality of the structure is caused almost entirely by the displacements of the metal atoms since the 62 oxygen atoms, within 0.05 Å, form a close-packed cluster of D_{3h} symmetry. In contrast to the molybdate, the corresponding "isostructural" tungstate, α-$P_2W_{18}O_{62}^{6-}$ (α-P_2W_{18}), is virtually nonchiral with all bridging W–O–W bonds of similar length.[3] An isomer of the tungstate, β-P_2W_{18}, has a closely related structure and is probably not significantly chiral.[4]

We have investigated the interaction of solutions of a number of related polyanions with *l*-brucine and *d*-cinchonine and have been able to demonstrate a significant Pfeiffer effect with P_2Mo_{18} and its two-electron reduction product. Only trivial amounts of optical activity were induced in nonchiral polyanions.

Experimental Section

Ammonium salts of P_2Mo_{18},[5] α-P_2W_{18},[5] β-P_2W_{18},[5] and tetrabutylammonium salts of $Mo_6O_{19}^{2-}$ (Mo_6)[6] and α-$SiMo_{12}O_{40}^{4-}$ ($SiMo_{12}$)[7] were prepared by published methods. Tetrabutylammonium and *l*-brucinium (bru^+) salts were obtained by precipitation from aqueous solution (pH ~0) with the corresponding hydrogen sulfates. Anal. Calcd for $[(C_4H_9)_4N]_5HP_2Mo_{18}O_{62}$: C, 24.05; H, 4.58; N, 1.75. Found: C, 23.94; H, 4.81; N, 1.73. Calcd for $(C_{23}H_{27}N_2O_4)_5HP_2Mo_{18}O_{62}$: C, 29.02; H, 2.89; N, 2.94. Found: C, 28.48; H, 3.28; N, 2.91. The two-electron blue $H_2P_2Mo^{V}{}_2MO_{16}O_{62}^{6-}$ was prepared by controlled potential electrolysis[8] or by chemical reduction with iron(II) sulfate in 1 M sulfuric acid. The tetrabutylammonium salt was isolated as above. Anal. Calcd for $[(C_4H_9)_4N]_5H_3P_2Mo_{18}O_{62}$: C, 24.04; H, 4.62; N, 1.75. Found: C, 22.02; H, 4.66; N, 1.62. The UV–visible spectra of the tetrabutylammonium salts in acetonitrile were in close agreement with those reported for aqueous solutions of the corresponding ammonium salts.

Spectroscopic measurements were made on Cary 14, Perkin-Elmer 457, and Jasco ORD/UV-5 instruments.

Results and Discussion

The infrared spectra of P_2Mo_{18}, reduced P_2Mo_{18}, and α-P_2W_{18} in the metal–oxygen stretching region are shown in Figure 2. Similar spectra for the oxidized anions have recently been reported by Tsvetkov and Karina.[9] Although the spectra

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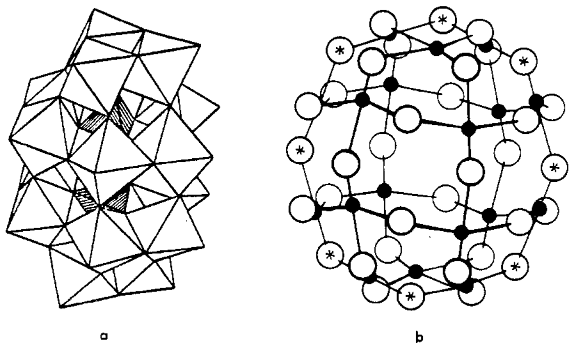

Figure 1. (a) Polyhedral representation of the structure of P_2Mo_{18} and α-P_2W_{18}. (b) A slightly exaggerated representation of the metal atom displacements in P_2Mo_{18}. Small dark circles are molybdenum atoms; large open circles are oxygens. Twenty-six oxygen atoms not shown, eight from two PO_4 tetrahedra inside, and eighteen terminal oxygens outside the polyhedral shell, complete distorted octahedra around each molybdenum. Multiple bonding to the external oxygens actually raises the metal atoms out of the MoO_4 planes shown, a detail that was omitted from the figure for reasons of clarity. The marked oxygens identify one of the three interpenetrating loops of alternately long and short Mo–O–Mo bonds mentioned in the text.

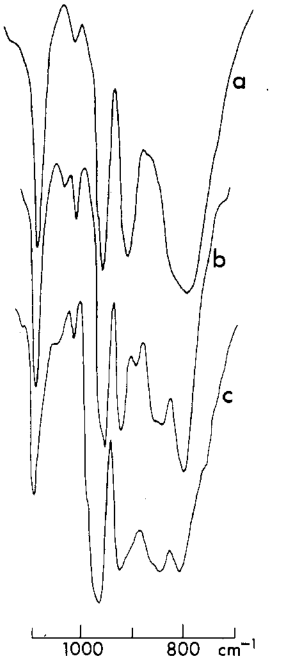

Figure 2. Infrared spectra (KBr pellets) of tetrabutylammonium salts of (a) α-P_2W_{18}, (b) P_2Mo_{18}, and (c) two-electron blue of P_2Mo_{18}.

of Figure 2 were recorded in KBr pellets, all the features shown were reproduced in spectra of solutions of the same anions in acetonitrile. The four prominent bands in the tungstate spectrum can be assigned by comparison with the spectrum of α-$PW_{12}O_{40}{}^{3-}$ (which it closely resembles):[10] 1095 cm^{-1}, ν(P–O); 965, ν(W–O, terminal); ~920, ν(W–O–W, octahedral edge-sharing); ~800, ν(W–O–W, octahedral corner-sharing). Both bands corresponding to M–O–M vibrations are clearly split in the spectrum of P_2Mo_{18}, and this is consistent with the presence of the unsymmetrical Mo–O–Mo bridges found in the structure of this anion. The splitting is less pronounced in the spectrum of the reduced anion, $H_2P_2Mo^V{}_2Mo_{16}O_{62}{}^{6-}$, an observation to be discussed below.

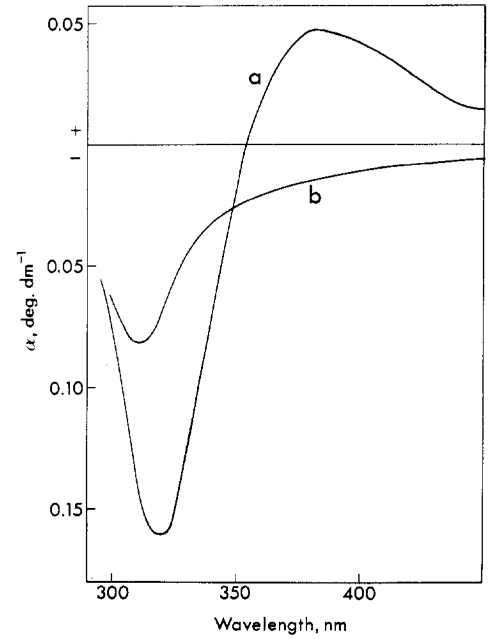

Figure 3. (a) ORD of 0.50 mM (l-bru)$_5HP_2Mo_{18}O_{62}$. (b) ORD of 2.50 mM l-brucine sulfate. Solvent is dimethylformamide.

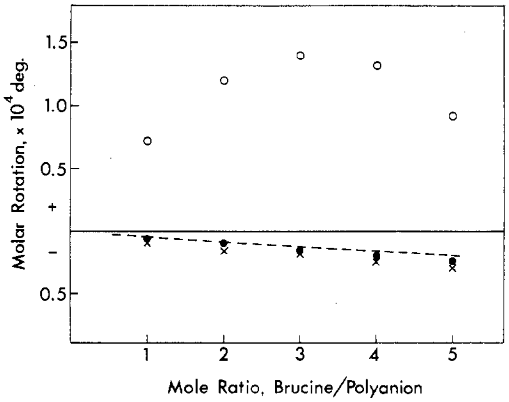

Figure 4. Optical rotation at 380 nm of polyanion solutions in the presence of varying amounts of l-brucine sulfate. Solvent is acetonitrile. Open circles are P_2Mo_{18}, closed circles are α-P_2W_{18}, and crosses are Mo_6. Broken line represents rotation of l-brucine sulfate alone.

Addition of l-brucine sulfate to an acidic solution containing P_2Mo_{18} yields a precipitate of (bru)$_5HP_2Mo_{18}O_{62}$. The optical rotatory dispersion (ORD) of this salt in dimethylformamide solution is shown in Figure 3 together with the ORD of an equivalent solution of brucine sulfate.[11] A Cotton effect at ca. 350 nm is clearly associated with a chromophore of the heteropoly anion which has its lowest energy electronic absorption at ca. 320 nm.[12] Similar and consistent ORD were observed for solutions of the tetrabutylammonium salt of P_2Mo_{18} in acetonitrile that contained varying proportions of brucine sulfate. The results of these experiments are summarized in Figure 4 which shows the molar rotations at the maximum of the Cotton effect centered at 350 nm. The maximum optical activity is observed at a brucine:P_2Mo_{18} ratio of about 3:1. Variations in the ORD at higher ratios can be quantitatively accounted for in terms of the increased brucine concentration.

Also shown in Figure 4 are the rotations of solutions of some other polyanions in the presence of brucine sulfate. It is well known that optical activity can be induced in nonchiral molecules or ions by the addition of a chiral species (solvent, potential ion-pairing or hydrogen-bonding partner, etc.).[13] In order to estimate the magnitude of such induced optical activity, experiments were carried out with α- and β-P_2W_{18}, α-$SiMo_{12}O_{40}{}^{4-}$ ($SiMo_{12}$), and $Mo_6O_{19}{}^{2-}$ (Mo_6). These anions were chosen because they have structures and charge densities similar to those of P_2Mo_{18} (and might therefore be expected to participate in ion pairing to a similar extent). Furthermore,

Table I. Optical Activity of Polyanion–Brucine Solutions[a]

Anion	Wavelength of lowest UV band, nm	Optical rotation at 380 nm[b]
P_2Mo_{18}	320	$+1.40 \times 10^3$
α-P_2W_{18}	295	-0.14×10^3
β-P_2W_{18}	295	-0.10×10^3
α-$SiMo_{12}$	310	-0.06×10^3
Mo_6	325	-0.19×10^3
None		-0.17×10^3

[a] 0.50 mM polyanion (as tetrabutylammonium salt); 1.50 mM *l*-brucine sulfate. Solvent is acetonitrile. [b] Deg M^{-1} dm^{-1} based on molarity of heteropolyanion. Uncertainty is $\pm 0.05 \times 10^3$.

all the anions absorb strongly between 295 and 325 nm. Solutions of the tetrabutylammonium salts of the above four anions in acetonitrile containing up to 5 mol of brucine sulfate/mol of heteropolyanion showed no new Cotton effects in the region 350–450 nm and only small differences in rotation from that of brucine sulfate alone. Typical values are given in Table I.

We conclude from these data that induced optical activity accounts for *at most* 10% of the phenomenon illustrated in Figure 3 and that therefore the P_2Mo_{18}–brucine solutions exhibited a Pfeiffer effect, i.e., displacement of a racemate equilibrium in favor of one enantiomer.[14] For a Pfeiffer effect to be observed, the racemic mixture must be optically labile. Interconversion of P_2Mo_{18} enantiomers could take place either by a dissociative mechanism (which would involve partial hydrolysis) or by an intramolecular rearrangement of short and long Mo–O–Mo bonds. The second mechanism merely requires displacement of the molybdenum atoms by about 0.4–0.5 Å and would account for the optical lability of P_2Mo_{18} in nonhydrolytic solvents such as acetonitrile. When *l*-brucine sulfate is added to aqueous or nonaqueous solutions of P_2Mo_{18}, partial or complete conversion to one enantiomer, $(+)_{380}$, is presumed to take place. Under conditions where the brucine salt of the heteropolyanion is soluble, i.e., in acetonitrile solution, a ratio of about 3 mol of brucine/mol of P_2Mo_{18} is apparently sufficient to cause complete conversion to the $(+)_{380}$ enantiomer.[15]

The net ORD of $(+)_{380}$-P_2Mo_{18}, obtained by subtracting the brucine rotations from a 5:1 brucine–polyanion mixture, is shown in Figure 5. The Cotton effect at 350 nm corresponds to the electronic absorption bands that have been assigned oxygen-to-molybdenum charge-transfer transitions.[16] Since the chirality of P_2Mo_{18} is dependent upon alternation in Mo–O–Mo bond lengths, it is not surprising that the charge-transfer transitions show high optical activity.

The corresponding ORD of the reduced anion, $H_2P_2Mo^V{}_2Mo_{16}O_{62}{}^{6-}$, obtained by similar methods to that of the oxidized anion, is also shown in Figure 5. Not only does the reduced anion have a diminished optical activity in the UV but no detectable Cotton effect is associated with the intervalence charge-transfer transitions at 600 and 750 nm.[17] The chirality of P_2Mo_{18} results from its constituent MoO_6 octahedra having symmetries far lower than C_{4v}. When Mo(VI) is reduced to Mo(V) in a heteropoly blue, the electron, according to ESR data,[18] occupies a formally nonbonding ("d_{xy}") orbital. It is therefore reasonable to suggest that the resulting Mo^VO_6 octahedron will more nearly approach C_{4v} symmetry and that as a result neighboring $Mo^{VI}O_6$ octahedra will also become less distorted. We have already pointed out (see Figure 2) that the infrared spectrum of the reduced anion shows less pronounced splitting of the bands attributed to Mo–O–Mo vibrations. The absence of any significant optical activity associated with the intervalence transitions is consistent with the localization of such transitions between neighboring metal atoms.[19]

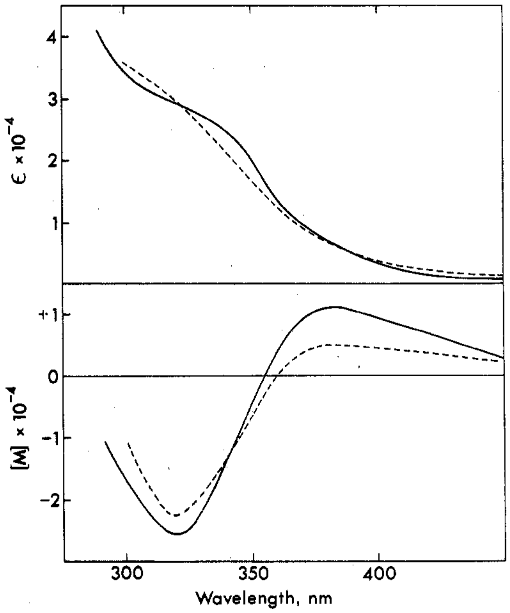

Figure 5. UV spectra and net Pfeiffer rotatory dispersion of P_2Mo_{18} (solid line) and $P_2Mo^V{}_2Mo_{16}$ (broken line) in the presence of *l*-brucine sulfate. Solvent is acetonitrile.

The general pattern of reduction of heteropolyanions to heteropoly blues, as revealed by polarography, is a sequence of two-electron additions. At appropriately high enough pH, i.e., under conditions where the reduced anions are not protonated, two-electron polarographic waves split into one-electron waves with half-wave potentials that are independent of pH.[20] The conventional interpretation of such behavior is that heteropoly blues containing even numbers of electrons are stabilized by antiferromagnetic spin pairing. Stabilization of odd reduction states appears to depend upon electrostatic factors; i.e., in the absence of protonation, reduction potentials will become successively more negative because the charge on the anion is increasing.

Unlike all other heteropolyanion–heteropoly blue systems (including that of α-P_2W_{18}), P_2Mo_{18} undergoes only two-electron reductions, *even under conditions where the reduced anions are not protonated*.[21] A thorough study by Contant and Fruchart[22] showed that only anions reduced by two, four, and six electrons (II, IV, and VI) were stable. A single odd reduction state, V, occurred in mixtures of IV and VI to a maximum proportion of about 50%. This behavior can be rationalized by assuming that the chiral distortion of P_2Mo_{18} must be partially overcome before the first electron transfer can occur. The energy required to overcome the distortion must therefore be at least as great as the expected *difference* between the first and second reduction potentials, $E(0 \rightarrow I) - E(I \rightarrow II) = \Delta E_{12}$. Some values[19,23] of ΔE_{12} for other heteropolyanions are 0.18 ($SiMo_{12}$), 0.24 (SiW_{12}), and 0.21 V (α-P_2W_{18}). We note that the difference between $E(0 \rightarrow I)$ for $SiMo_{12}$ and SiW_{12} is 0.47 V whereas the corresponding difference for P_2Mo_{18} $(0 \rightarrow II)$ and α-P_2W_{18} $(0 \rightarrow I)$ is only 0.30 V. This implies that $E(0 \rightarrow I)$ for P_2Mo_{18} is displaced toward a more negative potential by an amount (~0.17 V) which is sufficient to cause the first and second one-electron reductions to be superimposed. For all heteropolyanions ΔE_{23}, $E(I \rightarrow II) - E(II \rightarrow III)$, is greater than ΔE_{12} because the third electron is not stabilized by spin pairing. However, since we have shown that II is still chiral, an analogous argument to that put forward above can be used to explain why $E(II \rightarrow III)$ and $E(III \rightarrow IV)$ for P_2Mo_{18} are superimposed. In the more highly reduced anions, IV and VI, we presume that chirality of the P_2Mo_{18} structure has virtually disappeared so that the odd reduction state, V, is partially stabilized.

It is not clear why P_2Mo_{18} should adopt a different structure from that of P_2W_{18}.[24] Some years ago it was pointed out that most of the then known isopoly- and heteropolymolybdates have structures with two (cis) terminal oxygens per molybdenum, whereas most polytungstates have structures with a single terminal oxygen per tungsten.[25] Although there are exceptions to both generalizations, such exceptions are relatively few.[26] The structure of P_2Mo_{18} therefore appears to be a compromise between the limitations of stoichiometry and the tendency of molybdenum(VI) to adopt a cis dioxo coordination.

Acknowledgment. The partial support of this research by NIH Grant No. GM23263 is gratefully acknowledged.

Registry No. $[(C_4H_9)_4N]_5HP_2Mo_{18}O_{62}$, 66018-03-9; (*l*-bru)$_5HP_2Mo_{18}O_{62}$, 66018-02-8; $[(C_4H_9)_4N]_5H_3P_2Mo_{18}O_{62}$, 66018-01-7; α-$P_2W_{18}O_{62}{}^{6-}$, 12269-70-4; $Mo_6O_{19}{}^{2-}$, 11132-40-4; α-$SiMo_{12}O_{40}{}^{4-}$, 50927-64-5; *l*-brucine sulfate, 4845-99-2.

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(26) To date, the only confirmed exceptions are $Mo_6O_{19}{}^{2-}$, the Keggin anions $XMo_{12}O_{40}{}^{n-}$, X = P, As, Si, Ge (all monooxo terminal groups), $NiW_6O_{24}H_6{}^{4-}$, $NiW_6O_{24}{}^{8-}$, and probably $IW_6O_{24}{}^{5-}$ and $TeW_6O_{24}{}^{6-}$ (all cis dioxo terminal groups). Some polytungstates (e.g., $H_2W_{12}O_{42}{}^{10-}$) contain both dioxo and monooxo groups.

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Stereochemistry of Complex Inorganic Compounds. 36. Ammoniation Reactions of Some Optically Active 1,2-Dihalobis(ethylenediamine) Complexes of Rhodium(III) and Iridium(III) Ions

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Ammonation reactions of dihalobis(ethylenediamine) complexes of rhodium(III) and iridium(III) ions proceed with retention of configuration. The absolute configuration of optically active 1,2-dihalobis(ethylenediamine) complexes and their ammoniated complexes were inferred by comparison of the electronic and CD spectra of these complexes with those of the corresponding cobalt(III) complexes.

Introduction

The inversion of chiral 1,2-$[Co(en)_2Cl_2]^+$ has been observed to occur in the ammoniation reaction of the complex at liquid ammonia temperature.[2] In the reactions described in this paper, the ammoniation reactions of several dihalobis(ethylenediamine) complexes of rhodium(III) and iridium(III), including optically active complexes, were examined.

Experimental Section

A. Preparation of Complexes. The complexes 1,2-$[Co(en)_2Cl_2]Cl$,[3] 1,2-$[Co(en)_2(NH_3)Cl]Cl_2$,[4,5] 1,2- and 1,6-$[Co(en)_2(NH_3)_2](NO_3)_3$,[6] 1,2-$[Rh(en)_2Cl_2]Cl$,[7,8] 1,2- and 1,6-$[Rh(en)_2(NH_3)Cl](NO_3)_2$,[8] 1,6-$[Rh(en)_2Br_2]NO_3$,[8] 1,2- and 1,6-$[Rh(en)_2I_2]I$,[8] and 1,2- and 1,6-$[Ir(en)_2Cl_2]Cl$[9,10] were prepared as reported in the literature. 1,6-$[Rh(en)_2Cl_2]Cl$ was prepared by the method of Basolo et al.,[7,8] but the crystals obtained by the concentration of the aqueous solution were found to contain one molecule of water of crystallization. Anal. Calcd for $[Rh(en)_2Cl_2]Cl{\cdot}H_2O$: C, 13.83; H, 5.22; N, 16.12. Found: C, 13.87; H, 5.10; N, 16.38. The water of crystallization can be removed easily by heating the crystals at 100 °C for 30 min. Anal. Calcd for $[Rh(en)_2Cl_2]Cl$: C, 14.58; H, 4.87; N, 17.00. Found: C, 14.40; H, 4.95; N, 16.73.

1,2-$[Rh(en)_2Br_2]Br$. 1,2-$[Rh(en)_2Cl_2]Cl$ (0.65 g) was dissolved in 30 mL of water. After the addition of NaBr (1.5 g), the solution was refluxed for 30 min. Upon cooling the solution, yellow-orange crystals appeared. To complete the precipitation, 25 mL of ethanol and 25 mL of ether were added. A total of 0.48 g of 1,2-$[Rh(en)_2Br_2]Br$ was obtained. Anal. Calcd for $[Rh(en)_2Br_2]Br$: C, 10.38; H, 3.49; N, 12.11. Found: C, 10.81; H, 3.84; N, 12.23.

1,6-$[Rh(en)_2(NH_3)Br](NO_3)_2$. A solution of 1,6-$[Rh(en)_2Br_2]NO_3$ (0.57 g) in 30 mL of concentrated NH_4OH was refluxed for 30 min. After filtration, the filtrate was evaporated to dryness on a steam bath. The residue was dissolved in 3 mL of water. The solution was filtered and 3 mL of HNO_3 was added. After cooling, 50 mL of ethanol was carefully added. During the addition of ethanol, the desired yellow compound crystallized. This was collected, washed with ethanol and ether, and air-dried; yield 0.40 g. Anal. Calcd for $[Rh(en)_2(NH_3)Br](NO_3)_2$: C, 10.82; H, 4.31; N, 22.09. Found: C, 11.23; H, 4.43; N, 22.17.

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